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Nonlinear Optical Response of Titania Nanoparticles Prepared by Pulsed Laser Ablation

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Abstract

Titania nanoparticles were prepared by a Nd:YAG pulsed laser ablation in distilled water. The nanoparticles were characterized by UV/visible spectroscopy, transmission electron microscopy (TEM) and single beam z-scan technique. With the help of UV/vis. spectrum the band gap of the nanoparticles was calculated about 3.7eV for 0.75mj pulse energy. The average size of the nanoparticles was obtained about 14nm from TEM images. In addition the size distribution of the nanoparticles ranged from 5 to 50nm. The nonlinear index of refraction n_2 and nonlinear absorption coefficient β were measured using closed and open aperture z-scan technique respectively using CW He-Ne laser at various intensities.

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Z scan technique; Titania nanoparticles; Laser ablation; CW laser; TEM

1. Introduction

Nanoparticles (NPs) due to having a large surface-to-volume ratio and quantum confinement effect, they have unique optical, mechanical, electrical and chemical properties. In particular their nonlinear optical (NLO) response is enhanced remarkably with respect to the relative bulk materials[1]. Titanium oxide (Titania) NP as a wide-band gap semiconductor has been interesting from scientific standpoint because of its potential applications such as

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photocatalyst [2-4], solar cell [5], gas sensor [6], NLO materials [7-8]. Recently the NLO properties of materials containing titanium oxides have received attention [7, 9-10]. In the mentioned cases, pulsed lasers have been employed to study of NLO properties. In this article, we report NLO response of Titania NPs under continuous wave (CW) laser irradiation. The sample synthesis method is based on laser ablation, since it's an easy, fast and straightforward method for NPs generation as compared to other methods [11-12].

2. Experimental Detailes

2.1. Sample preparation

The colloidal solution of Titania NPs was achieved by pulsed laser ablation method following the literature procedure reported before [13]. A titanium plate was immersed in 2ml distilled water and ablated by a Nd:YAG laser (1064nm) with 240ns pulse duration, 2kHz repetition rate and 0.75 mJ pulse energy. The ablation process lasted 20 minutes to gain a condense solution suitable for nonlinearities study.

2.2. Characterization of the sample

Optical absorption spectrum was obtained using a Perkin Elmer Lambda25 model spectrometer with a resolution of 1nm in a wavelength ranging from 200 to 900nm. The band gap energy of the NPs was measured with the help of their optical absorption spectrum. For the direct band gap transition we have $\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}}$, known as Tauc relation. Where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the band gap energy and A is a constant. By plotting $(\alpha h\nu)^2$ versus $h\nu$ the band gap energy is obtained. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of E_g [14]

Moreover an EM 208 S Philips model transmission electron microscope operating at an accelerating voltage of 100kV was employed to perform electron microscopy analysis. The corresponding selected area electron diffraction (SAED) patterns reveal the crystalline structures of the Titania NPs.

The nonlinear index of refraction n_2 and absorption coefficient β were measured by closed-aperture and open aperture z-scan technique respectively, at the wavelength of 632.8nm, CW He-Ne laser . The experimental setup is shown in Fig.1.

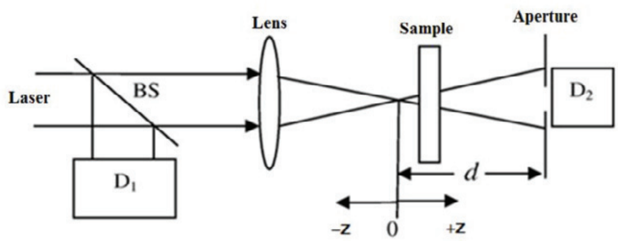


Fig. 1 Schematic of the experimental setup for closed-aperture

The nonlinear refraction index n_2 is obtained by measuring changes of the transmitted intensity of beam in the far field as a function of the sample position, Z. The required scan range in an experiment depends on the beam parameters and the sample thickness L. A critical parameter is the diffraction length, Z_0, of the focused beam defined as $\pi w_0^2/\lambda$ for a Gaussian beam where w_0 is the focal spot size (half-width at $\frac{1}{e^2}$ maximum in the irradiance). For thin samples i.e. $L \leq Z_0$, it is preferable to scan the sample for $\approx \pm 5Z_0$ or more. Typical values for aperture position range from $20Z_0$ to $100Z_0$. The size of aperture is signified by its transmittance, S, in the linear regime, i.e. when the sample has been placed far away from the focus.[15]. In our case S was about 0.064. Obviously S=1 for open z-scan schemes. For thin samples, by calculating ΔT_{p-v} , i.e. the difference between the peak and valley of normalized transmittance, we could obtain n_2 from this equation:

$$n_2 = \frac{\lambda\, \Delta T_{p-v}}{0.406\,(1-S)^{0.25} \times 2\pi I_0\, L_{eff}} \qquad (1)$$

Where I_0 is $\frac{2P_0}{\pi w_0^2}$, intensity of the beam at the focal point and L_{eff} , the effective thickness defined as $L_{eff} = \frac{1-e^{-\alpha L}}{L}$, where α is the linear absorption coefficient. For our case $\lambda = 632.8nm, w_0 = 36\ \mu m, L = 1mm$. In addition using the open aperture z-scan setup (S=1), the changes of the intensity transmittance of beam were measured while the sample was moved along the optical axis near the focal point. For $|q_0(Z,t)| = |\beta I_0(Z,t) L_{eff}| < 1$, the normalized transmittance can be expressed in a summation form:

$$T(Z, S=1) = \sum_{m=0}^{\infty} \frac{[-q_0(Z, t=0)]^m}{\left(1 + z^2/z_0^2\right)(m+1)^{\frac{3}{2}}} \qquad (2)$$

For small third-order nonlinear losses with response times much less than the pulse width (e.g. two-photon absorption, and for a Gaussian temporal shape pulse, the normalized change in transmittance energy $\Delta T(= T(Z) - 1)$ becomes

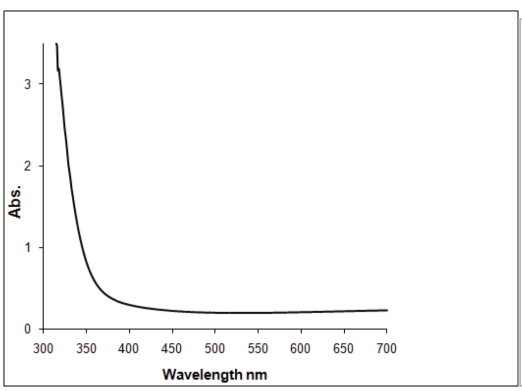
$$\Delta T(Z) \approx -\frac{q_0}{2\sqrt{2}} \frac{1}{\left[1 + Z^2/Z_0^2\right]} \qquad (3)$$

This mimics the Lorentzian distribution of the irradiance with Z for a focused Gaussian beam which is given by m=1 term in Eq. (2) [15-16]. By fitting experimental data with the theoretical Eq. (2) β is calculated.

3. Results and Discussion

3.1. Optical absorption

The UV/vis absorption of the colloidal Titania NPs have been shown in Fig.2. It shows a peak about 300nm. Also band gap energy of the NPs calculated using the plot of $(\alpha h\nu)^2$ versus the photon energy (Fig.3). The extrapolated E_g value is close to 3.7eV (i.e. $\lambda_1 cutoff \sim 334\ nm)$. The band gap of titanium oxides is 3.2eV. Generally the band gap could be wider than that of the bulk owing to the quantum size effect [18]



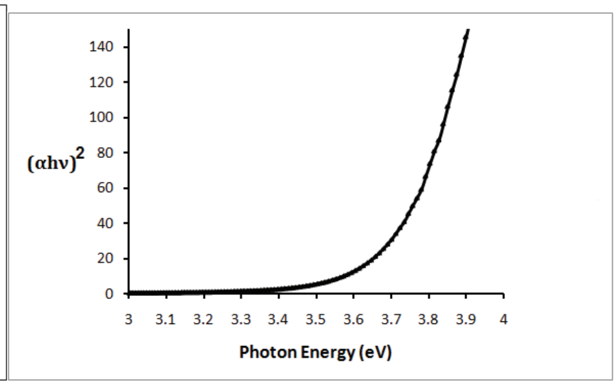


Fig.2 Absorption spectra of the colloidal TiO_2 NPs.

Fig.3 The plot of $(\alpha h\nu)^2$ versus $h\nu$ for the sample

3.2. Morphological observation

TEM and SAED images analysis (Fig. 4) shows that the synthesized NPs are in crystalline phase and their shapes are spherical and varying from 5 to 50nm. The average size is 14nm and maximum size distribution is at 10-15nm.

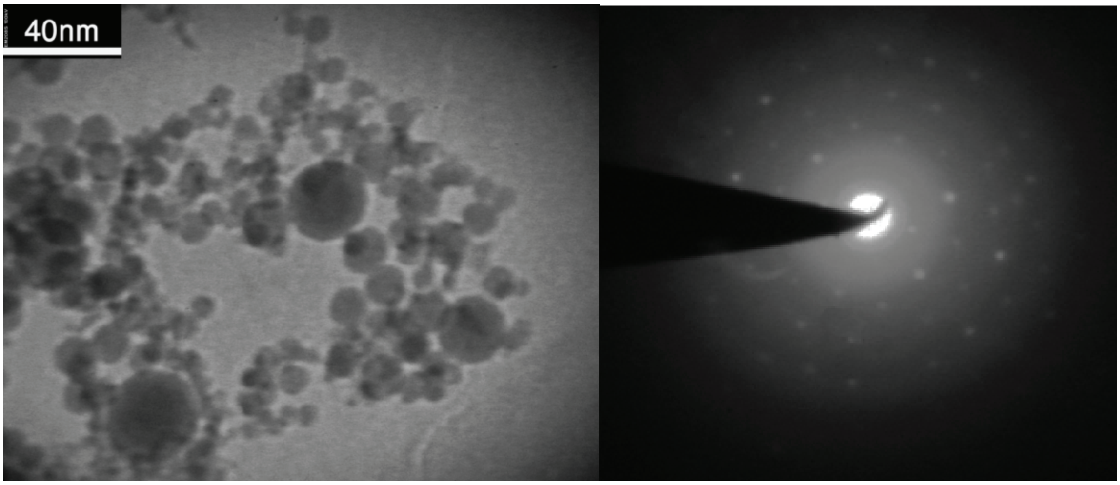


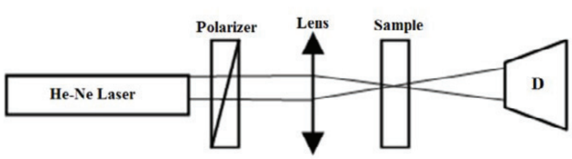
Fig.4 TEM (L) and SAED pattern (R) of the colloidal TiO_2 NPs

3.3. Linear absorption

The experimental setup for investigation of optical limiting behavior of the colloidal Titania NPs is shown in Fig.5. The linear absorption coefficient $\alpha = 1.92\ cm^{-1}$ was calculated by measuring the ratio of output power to input power and using following equation [17]:

$$\alpha = -\frac{1}{L} Ln\left(\frac{P_{out}}{P_{in}}\right)$$

Output power as a function of input power of the sample is shown in Fig. 6.



Figs.5 Schematic of the optical limiting setup

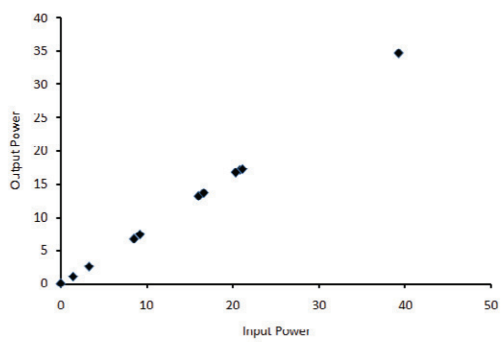


Fig.6 The plot of output power versus input power

3.4. The optical nonlinearities measurements

The optical refractive nonlinearity was measured by closed-aperture z-scan technique. A CW He-Ne laser at 632.8nm at 50mW was employed to study nonlinear properties. According to the normalized transmittance curves (Fig.7) the NPs act as a self-defocusing material. Since the peak of the curves precedes the valley, the sign of n_2 is negative. Moreover the Z-distance between peak and valley, ΔZ_{p-v} is about $1.7\ Z_0$, which is valid for closed-aperture Z-scan involving third-order nonlinearity.

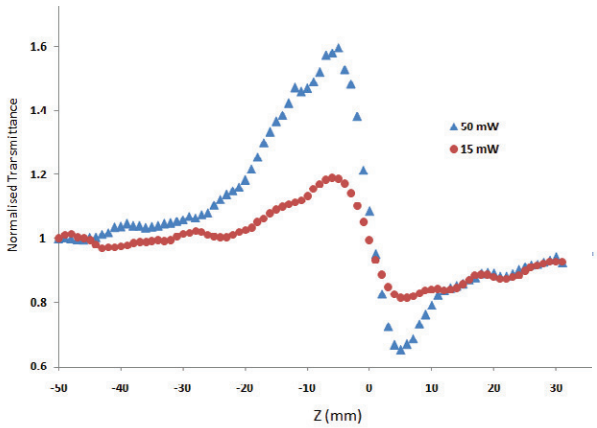


Fig.7 The closed-aperture z-scan result.

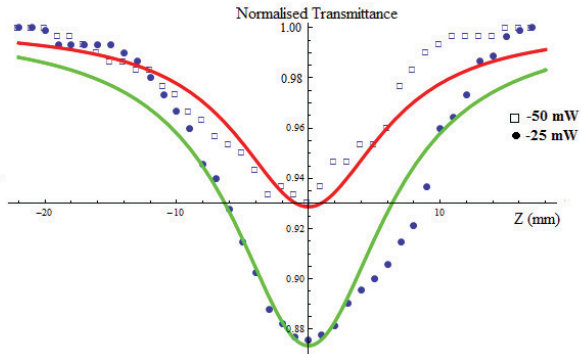


Fig. 8 The open-aperture z-scan result

The nonlinear absorption was evaluated by open-aperture z-scan technique. The experimental data points are fitted with equation (2) and β is taken as the fitting parameter. The gained data curves (Fig.8) shows the NPs have negative β, since they have a significant valley. This result suggested that this nonlinearity is mainly due to two-photon absorption phenomena [17]. The calculated values of nonlinear absorption coefficient β and nonlinear refractive index at two incident intensities are summarized in Table 1.

$P_0(mW)$	$Z_0(mm)$	$\Delta Z_{p-v}(mm)$	ΔT_{p-v}	$n_2\ (cm^2/W)$	$\beta\ (cm/W)$
15	6.43	12	0.37	0.35×10^{-11}	$\sim 6.5 \times 10^{-3}$
50	6.43	10	0.94	0.54×10^{-11}	$\sim 10^{-3}$

Table 1. Nonlinear coefficients of the Titania NPs as measured by Z-scan under CW He-Ne laser at 15 and 50 mW intensities.

Conclusion

We studied the morphology and optical characteristics of Titania nanoparticles synthesized by laser ablation method. UV/vis. spectroscopy allowed recognizing blue shift cutoff wavelength with respect to that of bulk. TEM analysis gave an estimation of 14nm for the average size of NPs. SAED pattern revealed the well crystalline structures of the sample. Using a CW He-Ne laser, the nonlinear refraction and absorption were investigated by closed and open aperture z-scan technique, respectively.

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